



Short communication

Compatibility of poly(bis(AEA4)-LiTFSI–MPPipTFSI ionic liquid gel polymer electrolyte with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ lithium ion battery anode

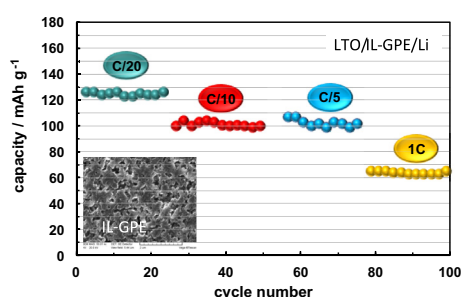
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HIGHLIGHTS

- Gel polymer electrolyte with MPPipTFSI was synthesized by photopolymerization method.
- IL gel polymer electrolyte as promising membrane for LTO anode.
- $\text{Li}_4\text{Ti}_5\text{O}_{12}$ /IL-GPE/Li cell shows a relatively high capacity of 124 mAh g^{-1} at 25°C .

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents the use of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) as anode with ionic liquid gel polymer electrolyte (IL-GPE) for application in lithium ion batteries. IL-GPE was obtained by in situ photopolymerization method of a mixture of ethoxylated bisphenol A diacrylate (bis(AEA4)) and 0.4 M solution of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPipTFSI). The surface morphology of the IL-GPE was studied using scanning electron microscopy (SEM). Stable, porous and flexible gel polymer electrolyte characterized high ionic conductivity (0.64 mS cm^{-1} at 25°C) and a wide electrochemical stability window (ESW) (4.8 V). The performances of LTO/IL-GPE/Li cell were tested by using cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge. Good charge/discharge capacities and low capacity loss at medium C rates preliminary cycling was obtained.

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1. Introduction

Nowadays, lithium ion batteries (LIBs) are used in many handheld and portable devices as a power source, such as in notebook computers, mobile phone, camera etc. Much effort is focused on the technology of lithium ion batteries for electric vehicles, hybrid electric vehicles and energy storage systems, which demand high

power, high energy density, fast charging, light weight, low costs and high safety standards.

Carbon or graphite is often used as negative electrode materials in conventional lithium ion batteries. However, the low Li^+ insertion voltage of carbon/graphite anodes during the charge process causes the formation of lithium dendrites on the anode surface. Alternative anode materials for lithium ion batteries can be $\text{Li}_4\text{Ti}_5\text{O}_{12}$ spinel (LTO), which has been intensively studied as one of the most promising anode materials for large size lithium ion batteries [1,3]. LTO has good Li^+ insertion and deinsertion reversibility with negligible change of the structure. It is a so-called “zero-strain” insertion host material during charge/discharge cycling [1]

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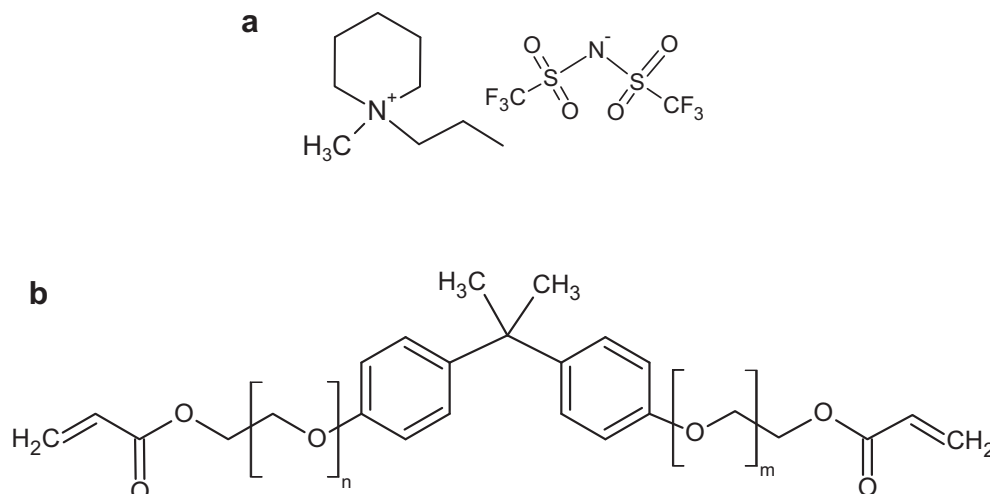


Fig. 1. Chemical structure of the a) MPPipTFSI b) bis(AEA4).

with a relatively high Li^+ voltage plateau at around 1.55 V vs. Li/Li^+ far above potential for metallic lithium formation, ensuring satisfactory safety, low cost and non-toxic [2–4]. The theoretical capacity of LTO is 175 mAh g^{-1} . The voltage operating range of LTO is more available to a wider group of electrolytes in view of their electrochemical stability, which is another advantage.

Apart from an anode and a cathode, in lithium batteries an electrolyte plays an important role. The electrolyte usually acts as a separator and ionic conductor between anode and cathode. Generally, it consists of salt, solvent, additive, separator and/or ion-conducting membrane or combination thereof [5]. One of the methods for creating electrolyte for the application in different energy storage devices is to place the liquid electrolyte in the polymeric matrix to form a gel polymer electrolyte (GPE). The ionic conduction mechanism in GPE should be very similar to that in liquid electrolyte, but gels have better shape flexibility over liquids [5]. Consequently, in recent times, GPEs are being intensively investigated for their use in electrochemical devices. They prevent leakage of liquid electrolyte and facilitate preparation of more flexible, smaller and thinner electrochemical devices. Presently, the most popular methods of GPE preparation include: (i) the solution casting method [6–8], (ii) the soaking method [9,10], (iii) the in situ polymerization method [11–15] and (iv) the electrospinning method [10,16].

On the other hand, ionic liquids (ILs) represent a group of interesting new class of fluids with the most attractive properties, such as non-volatility, non-flammability, high ionic density and conductivity, chemical and electrochemical stability, etc [17]. These attractive properties have led many scientists to exploit ILs as electrolytes in lithium ion batteries and other electrochemical devices [18].

Taking into account the advantages of both, a gel polymer electrolyte with an ionic liquid (IL-GPE) seems a good candidate to be used as an electrolyte in lithium ion batteries. In addition, photopolymerization appears to be one of the best methods of GPE preparation because of the short polymerization time (minutes or seconds) and low reaction temperature (room or ambient).

This paper presents the use of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) with porous ionic liquid gel polymer electrolyte (IL-GPE) for applications in lithium ion batteries. The IL-GPE was obtained by photochemical curing of the ethoxylated bisphenol A diacrylate (EO/phenol = 2) (bis(AEA4)) based system containing lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) and *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)

imide (MPPipTFSI). It was characterized by ionic conductivity in the temperature range of 5°C – 90°C , voltammetric methods, ac impedance spectroscopy and electrochemically tested combined with an $\text{Li}_4\text{Ti}_5\text{O}_{12}$ electrode. The resulting IL-GPE has sufficient mechanical properties and has fairly good compatibility with LTO anode and can be used as the electrolyte in lithium ion batteries.

2. Experimental

The *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (MPPipTFSI) was prepared by a reaction of *N*-methyl-*N*-propylpiperidinium bromide (MPPipBr) with lithium bis(trifluoromethanesulfonyl)imide (LiTFSI, Sigma–Aldrich) in an aqueous solution. MPPipBr was obtained from *N*-methylpiperidine (Sigma–Aldrich) and propylbromide (Sigma–Aldrich) dissolved in 2-propanol. The crude ionic liquid was washed with deionized water until no bromide anion was detected in the water. Subsequently, the obtained ionic liquid was dried under high vacuum for at least 48 h at 80°C . The water content of dried ionic liquid was analyzed based on the Karl–Fisher method (value was below 50 ppm). Fig. 1a shows the chemical structure of MPPipTFSI.

The Li–IL electrolyte was prepared by dissolving LiTFSI in MPPipTFSI at room temperature in an argon-filled glove box. The concentration of the lithium salt in IL was 0.4 M.

The IL-GPE was prepared by polymerization of a homogenous mixture consisting of bisphenol A ethoxylate diacrylate (EO/phenol = 2) (bis(AEA4); MW ~ 512, Sigma–Aldrich) and 0.4 M LiTFSI in MPPipTFSI solution at a 20:80 wt.%, and 1 wt.% of 2,2-dimethoxy-2-phenylacetophenone (photoinitiator, Sigma–Aldrich). The homogenous solution was spread between two PET foils and polymerized under UV light (400 W medium pressure Hg lamp, light intensity 2 mW cm^{-2}) in an argon filled glove box (H_2O content below 0.1% RH) for 10 min. The p(bis(AEA4))-(0.4 M LiTFSI–MPPipTFSI) (20:80 wt.%) IL-gel polymer electrolyte was obtained as a foil of ca. 0.02 cm in thickness. The chemical structure of the monomer (bis(AEA4)) is presented in Fig. 1b. The morphology of the IL-GPE was characterized by scanning electron microscopy (SEM, Tescan model Vega 5135). The accelerating voltage of the SEM was 20 kV.

The electrode film was prepared by casting on a Cu foil mixture of 80 wt.% active material ($\text{Li}_4\text{Ti}_5\text{O}_{12}$, Süd-ChemieAG, EXM 1037; specific capacity ca. 155 mAh g^{-1}), 10 wt.% acetylene black (AB, Sigma–Aldrich) and 10 wt.% poly(vinylidene difluoride) (PVdF,

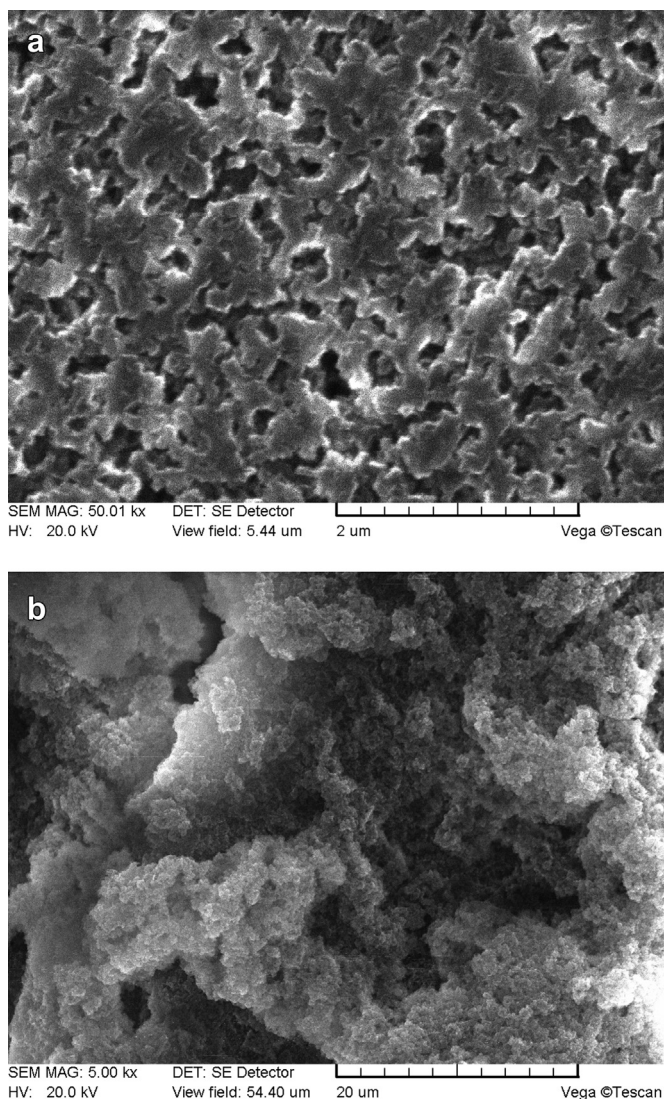


Fig. 2. SEM images of the a) surface and b) cross section of IL-GPE.

Sigma–Aldrich) dissolved in *N*-methyl-2-pyrrolidone (NMP, Aldrich). After evaporation of the solvent at mild heating, the electrode disc (area = 0.87 cm²) was dried under vacuum at 120 °C for at least 24 h. The average mass coating of the electrode was ca. 2 mg cm^{−2}.

The lithium polymer half-cell (Li₄Ti₅O₄/IL-GPE/Li) was assembled by placing in proper order: the Li₄Ti₅O₄ composite, an electrolyte film and a lithium metal disc in a test vessel (Swagelok® system). The cell system was prepared in a dry glove box.

The ionic conductivity of solutions (IL and Li–IL) and the gel polymer electrolyte was measured by the ac impedance method (EIS) using an impedance analyzer (μAutoLab FRA type III electrochemical system, EcoChemie, the Netherlands) over the frequency range from 1 Hz to 99 kHz with a potential amplitude of 5 mV. The measurements were carried out in the temperature range of 5 °C–90 °C. The IL-GPE was placed between two platinum blocking electrodes in a test vessel (Swagelok® system, the geometric area of the electrodes was 0.89 cm²). The ionic conductivity of solutions was measured in the conductivity cell, with two parallel platinum electrodes.

The electrochemical stability window (ESW) of IL-GPE was evaluated by linear sweep voltammetry (LSV) at scan rate of

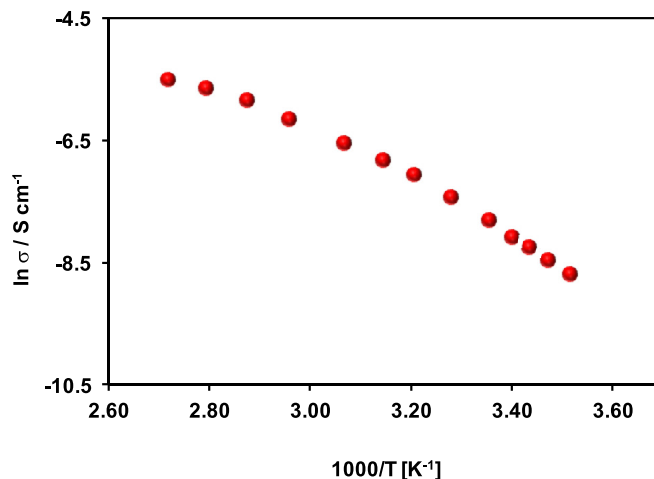


Fig. 3. The dependence of ionic conductivity on temperature for IL-GPE (p(bisAEA4)_{20%}–(0.4 M LiTFSI–MPPipTFSI)_{80%}).

5 mV s^{−1}. The measurement was performed using the μAutoLab system.

The electrochemical characteristic of the Li₄Ti₅O₄/IL-GPE/Li cell was investigated using cyclic voltammetry (CV), galvanostatic charge/discharge tests, and electrochemical impedance spectroscopy (EIS). The CV was performed using an electrochemical system (μAutoLab) in the voltage range of 1.0–2.5 V vs. Li/Li⁺ at scan rate of 0.01 mV s^{−1}. The galvanostatic charge/discharge tests were carried out using the Atlas 0461 MBI multichannel electrochemical system (Atlas–Sollich, Poland) in the voltage range of 1.0–2.5 V vs. Li/Li⁺ at various current rates from C/20 to 1C. All tests were conducted under ambient conditions.

3. Results and discussion

The surface morphology of IL-GPE (p(bisAEA4)_{20%}–(0.4 M LiTFSI–MPPipTFSI)_{80%}) obtained by photopolymerization is shown in Fig. 2a and b. As seen in the SEM images, the IL-GPE possesses a porous structure. As a result of UV-irradiation of the mixture, which includes the monomer and the solution of lithium salt in the ionic liquid, the porous polymer electrolyte was obtained. The pore size is suitable for the ion size of electrolyte, which in turn leads to the free movement of ions inside the polymer matrix. Moreover, due to the chemical structure of the bisAEA4 monomer (Fig. 1b), the resulting polymer matrix contains many ethylene oxide unit (EO) that may be helpful in the moving of lithium ions through its matrix. Other authors have also described the ability of EO unit in conduct of lithium ions through the matrix [19–22].

Fig. 3 presents the ionic conductivity variation for IL-GPE at temperature range from 5 °C to 90 °C. As seen in the figure, the IL-GPE conductivity is 0.64 at 25 °C and increases with temperature up to 3.8 mS cm^{−1} at 90 °C. The conductivity value of neat MPPipTFSI and 0.4 M LiTFSI–MPPipNTFS solution at 25 °C is equal to 1.6 and 0.86 mS cm^{−1}, respectively. These results are comparable with the literature data [8,23–25]. The conductivity of IL-GPE is lower than the conductivity of Li–IL solution, but it is not the most important parameter showing the usefulness of an electrolyte for use in LIBs.

The electrochemical stability of an electrolyte within the operation voltage of a battery system is very important for practical battery applications. Linear sweep voltammetry (LSV) has been used to investigate the electrochemical stability window (ESW) of IL-GPE. The LSV curves are shown in Fig. 4. The cathodic and anodic limiting potentials for IL-GPE are about 0.23 V and 5.0 V vs. Li/Li⁺,

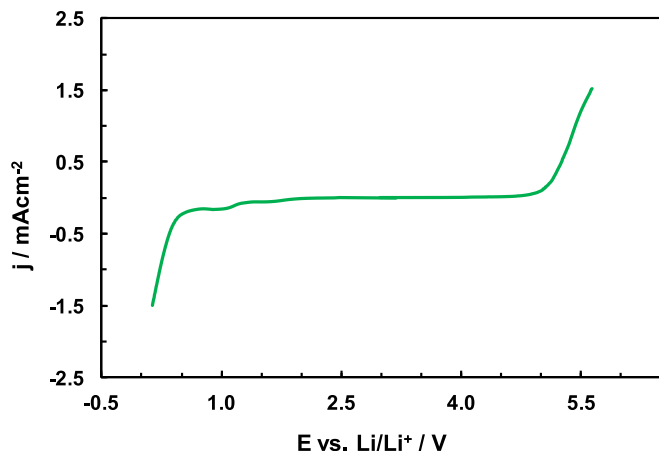


Fig. 4. Linear sweep voltammetry of IL-GPE (p(bisAEA4)₂₀–(0.4 M LiTFSI–MPPipTFSI)₈₀). Scan rate: 5 mV s^{−1} and 25 °C.

respectively, and ESW is ca. 4.8 V. These results suggest that p(bisAEA4)–(0.4 M LiTFSI–MPPipTFSI) (20:80 wt.%) gel polymer electrolyte is a good candidate to be safely used as an electrolyte in lithium-ion batteries with LTO anode and high voltage cathodes.

The cyclic voltammograms of the LTO electrode in a half-cell with IL-GPE is shown in Fig. 5. As can be seen in this figure, cathodic (Li⁺ insertion) and anodic (Li⁺ deinsertion) peaks are located at 1.48 V and 1.64 V, respectively. These peaks are very sharp and fairly symmetrical to each other, indicating excellent reversibility of Li ion insertion into and deinsertion from the LTO spinel and fast kinetics electrochemical process in the IL-GPE electrolyte. This is in a good agreement with the redox potential of the electrochemical process ($\text{Li}_4\text{Ti}_5\text{O}_{12} + 3\text{Li}^+ + 3\text{e}^- = \text{Li}_7\text{Ti}_5\text{O}_{12}$, $E = 1.55 \text{ V vs. Li/Li}^+$) determined from charging/discharging tests. The difference between the anodic and cathodic peak potential is about 0.24 V. The general shape of the CV voltammogram is similar to those previously reported by other authors [26–29].

Fig. 6 shows the galvanostatic voltage profile of the charge/discharge process of an LTO electrode with p(bisAEA4)₂₀–(0.4 M LiTFSI–MPPipTFSI)₈₀ electrolyte, at low current rate C/20 (25 °C). The charge/discharge voltage plateau occurs at around 1.44 V and

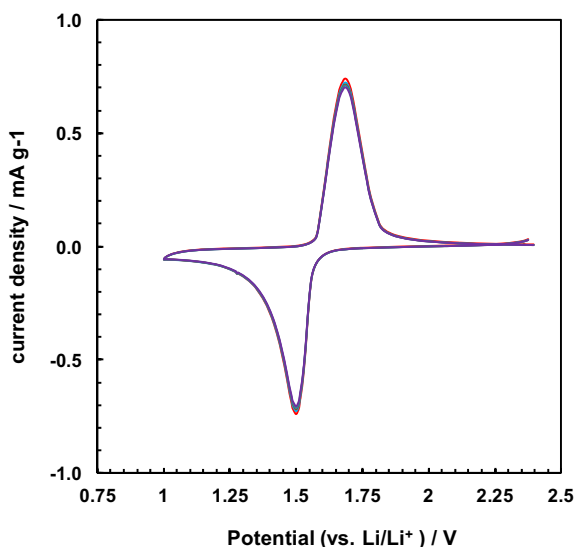


Fig. 5. Cyclic voltammetry for LTO/Li cell with IL-GPE vs. Li/Li⁺. Scan rate: 0.01 mV s^{−1}.

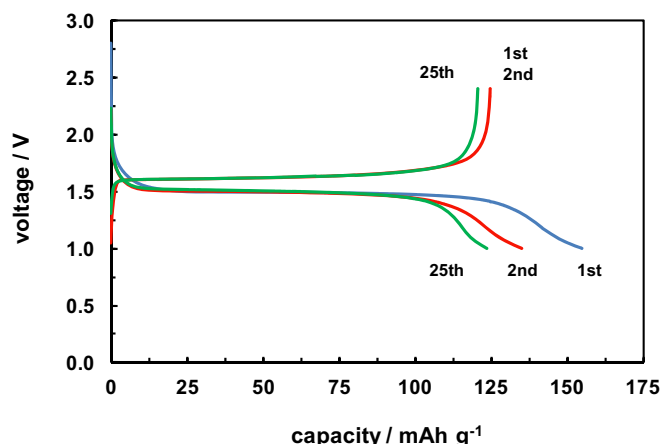


Fig. 6. Galvanostatic charge/discharge profile of LTO/IL-GPE/Li at C/20.

1.67 V vs. Li/Li⁺, respectively, which is also observed in conventional electrolytes. These results are in accordance with the value obtained in CV (Fig. 5). The initial discharge and charge capacities are 155 and 124 mAh g^{−1}, respectively. The observed loss of capacity may, in fact, be associated with the formation of the passivation layer on the electrodes surface in the first cycle. The initial coulombic efficiency is only 73%, but it quickly increases to 98% in the subsequent cycles. After 25 cycles, the specific capacity has reached a value of 120 mAh g^{−1}. The reversible capacity is not high and accounts for 68% of the theoretical value but 78% of capacity that was given by the producer of LTO (ca. 155 mAh g^{−1}), which is good result and promising prospects for further research.

The cell performance was tested by applied different current rates (C/20 to 1C). The corresponding cell performance is presented in Fig. 7. These results confirm the good cycle life capability of LTO/IL-GPE/Li cell and relatively high specific capacity, 124 mAh g^{−1} and 110 mAh g^{−1}, under low and medium C rates, respectively. Significant capacity decrease from 124 mAh g^{−1} (C/20) to 64 mAh g^{−1} was observed at 1C rate.

4. Conclusions

Ionic liquid gel polymer electrolyte was prepared using the in situ photopolymerization process. Good electrochemical stability (ESW is 4.8 V), high ionic conductivity (0.64 and 3.8 mS cm^{−1} at 25 °C and 90 °C, respectively), and fast method of preparation show

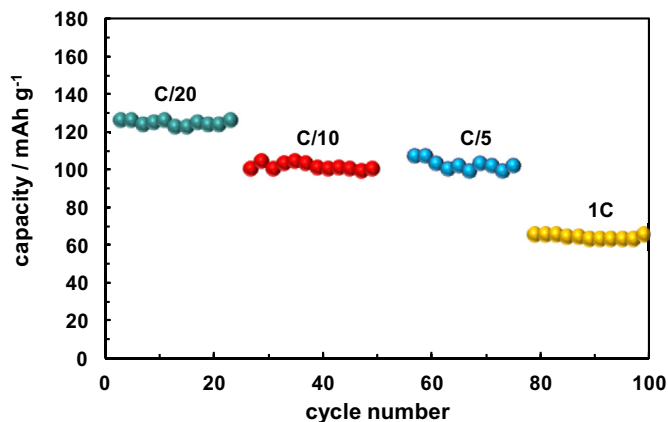


Fig. 7. Cycle performance of LTO/IL-GPE/Li cell at different C rates.

IL-GPE to be a good electrolyte for application in flexible lithium ion batteries.

Photopolymerization is confirmed as a suitable method for synthesizing porous gel polymer electrolytes. Compared to other techniques, it seems to be highly advantageous due to the ease and rapidity of processing.

Charge–discharge tests of LTO/IL-GPE/Li cell at different C rates exhibit a good specific capacity of 124 mAh g^{−1} and 110 mAh g^{−1} at C/20 and C/5, respectively. All obtained results show that the LTO/IL-GPE cell is a good candidate for use it in lithium ion batteries.

All the results obtained indicate that the ionic liquid gel polymer electrolyte and LTO anode may be successfully used in lithium ion batteries.

Acknowledgments

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